

# Exhibit C



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**Chaudhuri**

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**[54] SHAMPOO COMPOSITIONS WITH  
DIMETHICONE COPOLYOLS**

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**PCT Pub. Date:** **Jul. 9, 1992**

**[30] Foreign Application Priority Data**

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C11D 1/83; C11D 1/94**

**[52] U.S. Cl.:** **252/174.15; 252/547;  
252/174.21; 252/DIG. 1; 252/DIG. 7;  
252/DIG. 13**

**[58] Field of Search:** **252/DIG. 1, 174.15,  
252/174.21, DIG. 13, 547, DIG. 7; 424/70.12,  
70.121, 70.22, 70.28, 70.31**

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*Attorney, Agent, or Firm*—Stephen P. Williams

**[57] ABSTRACT**

A conditioning shampoo composition comprises, as the conditioning agents thereof, from 0.1 to 4.0% by weight of one or more dimethicone copolyols having an ethylene oxide/propylene oxide (EO/PO) ratio of from 20/80 to 80/20 and from 0.5 to 4.0% by weight of one or more non-ionic emulsifiers having an HLB of from 8 to 12 and which do not affect the foaming property of the shampoo.

**7 Claims, No Drawings**

## SHAMPOO COMPOSITIONS WITH DIMETHICONE COPOLYOLS

This invention is concerned with shampoo compositions and, more particularly, with conditioning shampoos, that is shampoos which have both the usual cleansing action and also a conditioning action. The use of such shampoos avoids the necessity for the separate use of a hair conditioner after the hair has been washed with a conventional shampoo having only a cleansing action.

Whilst conditioning shampoo compositions are known, a disadvantage that arises with some of them is that on repeated use, there is a build up of the conditioning ingredients on the hair so that the washed hair no longer feels pleasant to the user.

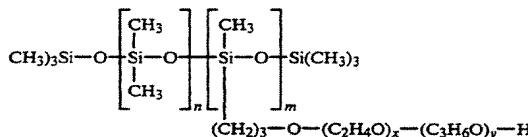
Conditioning shampoos have also been described and are commercially available which do not suffer from this disadvantage, that is the build up of conditioning agents. Such shampoo compositions are described for example, in U.S. Pat. Nos. 4,704,272; 4,741,855; and 4,788,006 and in British Specifications 2,192,194A and 2,196,980A.

An object of the present invention is to provide alternative conditioning shampoo compositions which are not subject to the significant build up of conditioning ingredients on repeated use.

We have found that these requirements can be met by using a combination of certain dimethicone copolyols and certain non-ionic emulsifiers having an HLB of from 8 to 12 as the conditioning agents in a shampoo composition which may, in other respects, be conventional.

According to the present invention, there is provided a conditioning shampoo composition which comprises, as the conditioning agents thereof, from 0.1 to 4.0% by weight of one or more dimethicone copolyols having an ethylene oxide/propylene oxide (EO/PO) ratio of from 20/80 to 80/20 and from 0.5 to 4.0% by weight of one or more non-ionic emulsifiers having an HLB of from 8 to 12 and which do not affect the foaming property of the shampoo.

Dimethicone copolyol is a CTFA adopted name for polysiloxane polyether copolymers of the formula:



where n, m, x and y are integers. The dimethicone copolyols used according to the invention have values of x and y such that the ratio x:y, that is the EO/PO ratio, is from 20/80 to 80/20.

Preferred dimethicone copolyols contain from 60 to 140 SiO<sub>2</sub> units, that is the sum of n and m is from 60 to 140.

The dimethicone copolyol constituent of the shampoo composition preferably comprises a major proportion of a dimethicone copolyol having an EO/PO ratio of from 80/20 to 70/30 and a minor proportion of a dimethicone copolyol having an EO/PO ratio of from 20/80 to 40/60.

Suitable dimethicone copolyols for use in the shampoo compositions according to the invention are avail-

able, for example, from Th. Goldschmidt AG, of Essen, Germany under the Trade Mark "Abil". A preferred dimethicone copolyol having an EO/PO ratio of 77/23 is available as "Abil" B88183 and a preferred dimethicone copolyol having an EO/PO ratio of 20/80 is available as "Abil" B8852; these two materials both contain about 60 SiO<sub>2</sub> units. A preferred dimethicone copolyol having an EO/PO ratio of 40/60 and containing about 140 SiO<sub>2</sub> units is available as "Abil" G911.

We have found that the extent of deposition of the dimethicone copolyol can be controlled by using it in conjunction with the non-ionic emulsifier having an HLB of from 8 to 12; in this way excessive build up of the conditioning agent on repeated use of the shampoo can be prevented. The greater the amount of the non-ionic emulsifier used, in relation to a given amount of dimethicone copolyol, the less of the latter is left on the hair.

For any particular choice of dimethicone copolyol(s) and non-ionic emulsifier(s), the optimum proportions of these two ingredients to obtain the desired deposition of dimethicone copolyol on the hair can be readily established by routine experimentation. By way of example, using a preferred combination of dimethicone copolyols as referred to above and the particularly preferred non-ionic emulsifier referred to below, we have found that an optimum level of dimethicone copolyol deposition is obtained by using 1.5% by weight of the non-ionic emulsifier and 1.1% by weight of the dimethicone copolyol combination.

Preferred non-ionic emulsifiers having an HLB of from 8 to 12 for use in accordance with the invention are:

CTFA name	Trade name	Chemical name	HLB
Sorbitan laurate	Arlacel 20	Sorbitol mono-laurate	8.6
PEG30 castor oil	Arlatone 827	Ethoxylated castor oil	11.9
PEG25 hydrogenated castor oil	Arlatone G	POE(25) hydrogenated castor oil	10.8
PEG40 sorbitan peroleate	Arlatone T	POE(40) sorbitol haptaleate	9.5
PEG40 sorbitan hexaoleate	Atlas G1086	POE(40) sorbitol hexaoleate	10.2
n/a	Atlas G1087	POE sorbitol oleate	10.2
n/a	Atlas G1096	POE sorbitol hexaoleate	11.4
n/a	Atlas G1281	POE triglyceride	9.7

n/a = not available. (All supplied by ICI Speciality Chemicals).

Of these, PEG40 sorbitan hexaoleate is particularly preferred.

The shampoo composition according to the invention will contain cleansing agents which may be any of the anionic, cationic, amphoteric and non-ionic surfactants conventionally used in such compositions, these ingredients being used in the conventional proportions. The composition can, and usually will, contain further ingredients which provide particular desired characteristics or properties to the composition.

Suitable ingredients for shampoo compositions according to the invention are, for example, as follows:

Cleansing agents

It is preferred that the cationic component of the surfactants included in the composition should be one or more quaternary ammonium salt surfactants. A num-

ber of quaternary surfactants can be used for this purpose; preferred compounds are, for example, stearamidopropyl dimethylamine lactate and steartrimonium hydrolysed animal protein (available under the Trade Mark "Crotein Q" from Croda Chemicals).

The proportion of quaternary surfactant used is preferably from 0.5 to 2.0% by weight.

It is preferred that the composition should contain from 10 to 20% by weight of one or more anionic surfactants, such as sodium laureth sulphate and ammonium lauryl sulphate, and from 1 to 5% by weight of one or more amphoteric surfactants, such as cocamidopropyl betaine, as the main cleansing agents. Thickeners

Suitable thickeners include, for example, hydroxypropyl methyl cellulose and talloweth 60 myristyl glycol; the proportion of thickener is suitably from 0.1 to 2.0% by weight, depending on the type of thickener used and the required viscosity. Hair bodying agents

Suitable agents for imparting body to the hair include, for example, cetyl alcohol and lauric acid monoglyceride; these agents are suitably used in a proportion of from 0.50 to 1.50% by weight.

Other conventional ingredients which may be and preferably are included in the shampoo composition are: a hydrotrope, such as ammonium xylene sulphonate, to prevent deposition in hard water areas of undesirable materials on the hair; pearlisising agents; preservatives; pH adjusters, such as lactic acid; colourants; and perfumes.

In order that the invention may be more fully understood, the following examples, in which all percentages are by weight, are given by way of illustration only.

### EXAMPLES 1-3

Three conditioning shampoo compositions were made up having the compositions set out in Table 1.

TABLE 1

Example	% active		
	1	2	3
Sodium laureth sulphate	7.00	7.00	7.00
Ammonium lauryl sulphate	7.00	7.00	7.00
Cocamidopropyl betaine	1.60	1.60	1.60
Ammonium xylene sulphonate	1.40	1.40	1.40
PEG40 sorbitan hexaoate	1.50	1.50	1.50
Dimethicone copolyol (Abil B88183)	1.00	1.00	1.00
Dimethicone copolyol (Abil B8852)	1.10	1.10	—
Dimethicone copolyol (Abil G911)	—	—	0.10
Stearamidopropyl dimethyl- amine lactate	0.625	0.625	0.625
Cetyl alcohol	0.50	0.50	0.50
Na laureth sulphate (and) glycol distearate (and) cocamide MEA	0.90	0.90	0.90
Hydroxypropyl methyl cellulose	0.25	0.25	0.25
Methylchloroisothiazolinone	0.0009	0.0009	0.0009
Talloweth 60 myristyl glycol	0.45	—	—
Lauric acid monoglyceride	—	1.50	1.50
Lactic acid	—	0.20	0.20
Colour, perfume and water	to 100	to 100	to 100

These shampoo compositions were used by a professional hairdresser to wash hair in comparison with a commercially available conditioning shampoo (used as a control).

Each person having their hair washed had one half of their head (left or right) washed with one of the test shampoos and the other half washed with the control shampoo. The shampoos, that is the test shampoo and the control shampoo, were provided to the hairdresser in syringes containing 7 ml of shampoo. The syringes

were labelled with the test persons name, date, time of appointment and side of head on which the shampoo was to be used. Neither the test person nor the hairdresser knew which shampoo (that is test shampoo or control shampoo) was present in each syringe.

Each test shampoo was tested on a panel of 60 subjects.

During and after the hair washing operation, the hairdresser made an assessment on both sides of the head using a five point scale (5=excellent, 4=very good, 3=good, 2=fair and 1=poor) for each of the following fifteen attributes:

- initial lather
- quantity of lather
- quality of lather
- cleanliness of wet hair
- ease of rinsing
- ease of wet combing
- ease of dry combing
- flyaway
- hair manageability
- softness
- silkeness
- condition of hair
- body
- feel of dry hair
- shine

The average ratings of the shampoo of Example 1 over the whole of the test panel were in the range 4.06-5.00, those of the shampoo of Example 2 were in the range 4.28-5.00, and those of the shampoo of Example 3 were in the range 4.32-5.0 (for comparison the ratings of the control shampoo were in the range 4.24-5.00).

It is claimed:

1. A conditioning shampoo composition which comprises in percent by weight in water 10 to 20% of one or more anionic surfactants, 1 to 5% of one or more amphoteric surfactants, 0.5 to 2.0% of one or more quaternary ammonium surfactants, 0.5 to 4.0% of one or more non-ionic emulsifiers having an HLB of from 8 to 12, and 0.1 to 4.0% of one or more dimethicone copolyols having from 60 to 140 SiO<sub>2</sub> units and an ethylene oxide/propylene oxide (EO/PO) ratio of from 20/80 to 80/20.

2. A shampoo composition according to claim 1 wherein the dimethicone copolyol comprises a major proportion of a dimethicone copolyol having an EO/PO ratio of from 80/20 to 70/30 and a minor proportion of a dimethicone copolyol having an EO/PO ratio of from 20/80 to 40/60.

3. A shampoo composition according to claim 2 comprising 1.1% dimethicone copolyol and 1.5% non-ionic emulsifier.

4. A shampoo composition according to claim 1, in which the non-ionic emulsifier having an HLB of from 8 to 12 is polyethylene glycol (PEG) 40 sorbitan hexaoate.

5. A shampoo composition according to claim 1 in which the dimethicone copolyol has an EO/PO ratio of 77/33.

6. A shampoo composition according to claim 1, in which the quaternary surfactant is stearamidopropyl dimethylamine lactate or steartrimonium hydrolysed animal protein.

7. A shampoo composition according to claim 1 comprising 1.1% dimethicone copolyol and 1.5% non-ionic emulsifier.

\* \* \* \* \*



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(12) **United States Patent**  
Hughes

(10) **Patent No.:** US 6,294,154 B1  
(45) **Date of Patent:** \*Sep. 25, 2001

(54) **ORAL COMPOSITIONS CONTAINING  
DIMETHICONE COPOLYOLS**

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(\*) Notice: This patent issued on a continued prosecution application filed under 37 CFR 1.53(d), and is subject to the twenty year patent term provisions of 35 U.S.C. 154(a)(2).

Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

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A61K 7/30; A61K 9/68**

(52) U.S. Cl. ..... **424/49; 424/52; 424/440;  
424/48**

(58) **Field of Search** ..... 424/49-58

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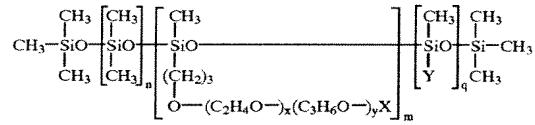
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Primary Examiner—Shep K. Rose

(57) **ABSTRACT**

An oral composition in the form of a toothpaste, powder, liquid dentifrice, mouthwash, denture cleanser, chewing gum or candy comprising a lipophilic compound selected from flavorants, physiological cooling agents and antimicrobial compounds and a dimethicone copolyol selected from alkyl- and alkoxy-dimethicone copolyols having the formula (I):



wherein X is selected from hydrogen, alkyl, alkoxy and acyl groups having from about 1 to about 16 carbon atoms, Y is selected from alkyl and alkoxy groups having from about 8 to about 22 carbon atoms, n is from about 0 to about 200, m is from about 1 to about 40, q is from about 1 to about 100, the molecular weight of the residue  $(\text{C}_2\text{H}_4\text{O})_x(\text{C}_3\text{H}_6\text{O})_y$  X is from about 50 to about 2000, and x and y are such that the weight ratio of oxyethylene:oxypropylene is from about 100:0 to about 0:100. The composition provides improved antiplaque and anti-bacterial activity together with enhanced substantivity, impact and/or efficacy of the lipophilic components on teeth or dentures.

**10 Claims, No Drawings**

## 1

ORAL COMPOSITIONS CONTAINING  
DIMETHICONE COPOLYOLS

## TECHNICAL FIELD

The present invention relates to oral compositions such as toothpastes, toothpowders, liquid dentifrices, mouthwashes, denture cleansers, chewing gums, candies and the like. In particular, the invention relates to oral compositions having enhanced antiplaque activity together with excellent cleansing performance, physical characteristics, and in-use performance characteristics.

## BACKGROUND

Plaque is initiated when bacteria adhered to pellicle form a proteinaceous film on the surface of teeth. The adherent bacteria metabolize dietary constituents and reproduce and aggregate to form the tenacious deposit known as plaque. Plaque generally consists of bacteria, bacterial end products such as polysaccharides, inorganic salts and salivary proteins. Plaque bacteria ferment dietary carbohydrates to organic acids which demineralize enamel resulting in tooth decay.

Calculus is essentially plaque that has been mineralized with calcium phosphates salts. As calculus matures and hardens, it tends to stain noticeably due to adsorption of dietary chromagens. In addition to their unattractive appearance, calculus deposits at the gum line are a contributing source of gingivitis and periodontal disease. Besides the hygienic and health problems resulting from plaque, research has shown that the primary source of bad breath is the retention and subsequent degradation of dead cellular material sloughed off continuously by the normal, healthy mouth.

Modern dental hygiene and denture preparations typically contain antiplaque and/or antitartar agents, as well as antimicrobial agents and flavorants. Antimicrobial action could affect plaque formation by either reducing the number of bacteria in the mouth/dentures or by killing those bacteria trapped in the film to prevent further growth and metabolism.

Flavorants may alleviate the problem of bad breath via a deodorizing action. Some antimicrobial agents, e.g. menthol may, also serve as breath deodorizers. However, the efficacy of antimicrobial agents depends largely on their intraoral/denture retention, particularly their retention on the surface of the teeth or dentures where plaque is formed.

A typical disadvantage of known dental preparations is that only a relatively short time during which the teeth are being cleaned or the mouth is being rinsed is available for antimicrobial agents in the preparations to take effect. The problem is compounded by the fact that dentifrice preparations are used infrequently: most are used once or, perhaps, twice daily. Consequently, the long time period between brushings for a majority of the population provides optimum plaque forming conditions.

There has been a need, therefore, for developing an oral formulation which has a prolonged, residual antimicrobial and/or flavor impact effect.

It is known to include silicones in dentifrice compositions, allegedly to coat the teeth and prevent cavities and staining. For instance, GB-A-689,679 discloses a mouthwash containing an organopolysiloxane for preventing adhesion of, or for removing tars, stains, tartar and food particles from the teeth. The mouthwash may include anti-septic compounds, such as thymol, and flavoring and perfume agents.

## 2

U.S. Pat. No. 2,806,814 discloses dental preparations including, in combination, a higher aliphatic acyl amide of an amino carboxylic acid compound as an active and a silicone compound. The patent notes that silicone compounds have been proposed for prevention of adhesion or to facilitate the removal of tars, stains, tartar and the like from teeth. The silicone compound is said to act as a synergist in improving the antibacterial and acid inhibiting activity of the active ingredient. Dimethyl polysiloxanes are said to be particularly effective. Flavoring oils and/or menthol may be included.

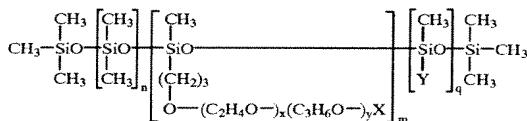
U.S. Pat. No. 3624120 discloses quaternary ammonium salts of cyclic siloxane polymers for use as cationic surfactants, bactericides and as anticariogenic agents.

Accordingly, the present invention provides oral compositions having improved efficacy on plaque, mucilaginous and bacterial deposits and which at the same time provides excellent cleansing performance, physical characteristics, and in-use performance characteristics.

The invention further provides oral compositions containing a lipophilic compound such as a flavorant, physiological cooling agent or antimicrobial, and which has improved substantivity, impact and/or efficacy on teeth and dentures.

## SUMMARY OF THE INVENTION

According to a first aspect of the invention, there is provided an oral composition in the form of a toothpaste, powder, liquid dentifrice, mouthwash, denture cleanser, chewing gum or candy comprising one or more oral composition components selected from abrasives, binders, humectants, surfactants, fluoride ion sources, anti-calculus agents and sweeteners and additionally comprising a dimethicone copolyol selected from alkyl- and alkoxy-dimethicone copolyols having the formula (I):



wherein X is selected from hydrogen, alkyl, alkoxy and acyl groups having from about 1 to about 16 carbon atoms, Y is selected from alkyl and alkoxy groups having from about 8 to about 22 carbon atoms, n is from about 0 to about 200, m is from about 1 to about 40, q is from about 1 to about 100, the molecular weight of the residue  $(\text{C}_2\text{H}_4\text{O})_x(\text{C}_3\text{H}_6\text{O})_y$  is from about 50 to about 2000, preferably from about 250 to about 1000 and x and y are such that the weight ratio of oxyethylene:oxypropylene is from about 100:0 to about 0:100, preferably from about 100:0 to about 20:80.

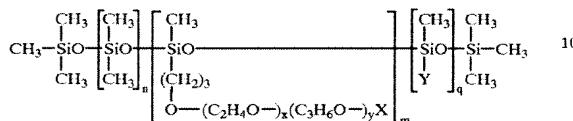
According to a further aspect of the invention, there is provided an oral composition in the form of a toothpaste, powder, liquid dentifrice, mouthwash, denture cleanser, chewing gum or candy comprising a lipophilic compound selected from flavorants, physiological cooling agents and antimicrobial compounds and a dimethicone copolyol selected from alkyl- and alkoxy-dimethicone copolyols having the formula (I).

All percentages and ratios herein are by weight of total composition, unless otherwise indicated.

The oral composition of the invention thus comprise a dimethicone copolyol antiplaque agent while preferred compositions additionally comprise a lipophilic compound and/or one or more oral composition components selected from

abrasives, binders, humectants, surfactants, fluoride ion sources, anti-calculus agents and sweeteners. Each of these will be discussed in turn.

In general terms, the dimethicone copolyol is selected from alkyl- and alkoxy-dimethicone copolyols having the formula (I):



wherein X is selected from hydrogen, alkyl, alkoxy and acyl groups having from about 1 to about 16 carbon atoms, Y is selected from alkyl and alkoxy groups having from about 8 to about 22 carbon atoms, n is from about 0 to about 200, m is from about 1 to about 40, q is from about 1 to about 100, the molecular weight of the residue  $(\text{C}_2\text{H}_4\text{O})_x(\text{C}_3\text{H}_6\text{O})_y$ , X is from about 50 to about 2000, preferably from about 250 to about 1000 and x and y are such that the weight ratio of oxyethylene:oxypropylene is from about 100:0 to about 0:100, preferably from about 100:0 to about 20:80.

In preferred embodiments, the dimethicone copolyol is selected from  $\text{C}_{12}$  to  $\text{C}_{20}$  alkyl dimethicone copolyols and mixtures thereof. Highly preferred is cetyl dimethicone copolyol marketed under the Trade Name Abil EM90. The dimethicone copolyol is generally present in a level of from about 0.01% to about 25%, preferably from about 0.1% to about 5%, more preferably from about 0.5% to about 1.5% by weight.

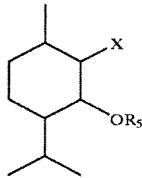
The oral compositions of the invention preferably also include a lipophilic compound. In general terms, lipophilic compounds suitable for use herein are oil-like materials which are soluble or solubilisable in the dimethicone copolyol, preferably at a level of at least about 1%, more preferably at least about 5% by weight at 25° C. Preferred lipophilic compounds are selected from flavorants, physiological cooling agents and antimicrobial compounds. The dimethicone copolyol acts to enhance the substantivity of the lipophilic compound to teeth and/or dentures, thereby providing enhanced and/or sustained flavor impact and antimicrobial efficacy.

Lipophilic flavorants suitable for use herein comprise one or more flavor components selected from wintergreen oil, oregano oil, bay leaf oil, peppermint oil, spearmint oil, clove oil, sage oil, sassafras oil, lemon oil, orange oil, anise oil, benzaldehyde, bitter almond oil, camphor, cedar leaf oil, marjoram oil, citronella oil, lavender oil, mustard oil, pine oil, pine needle oil, rosemary oil, thyme oil, cinnamon leaf oil, and mixtures thereof.

Lipophilic antimicrobial compounds suitable for use herein include thymol, menthol, triclosan, 4-hexylresorcinol, phenol, eucalyptol, benzoic acid, benzoyl peroxide, butyl paraben, methyl paraben, propyl paraben, salicylamides, and mixtures thereof.

Physiological cooling agent suitable for use herein include carboxamides, menthane esters and menthane ethers, and mixtures thereof.

Suitable menthane ethers for use herein are selected from those with the formula:



where R<sub>5</sub> is an optionally hydroxy substituted aliphatic radical containing up to 25 carbon atoms, preferably up to 5 carbon atoms, and where X is hydrogen or hydroxy, such as those commercially available under the trade name Takasago, from Takasago International Corporation. A particularly preferred cooling agent for use in the compositions of the present invention is Takasago 10 [3-1-menthoxy propan-1,2-diol (MPD)]. MPD is a monoglycerin derivative of 1-menthol and has excellent cooling activity.

The carboxamides found most useful are those described in U.S. Pat. No. 4,136,163, Jan. 23, 1979 to Wason et al., and U.S. Pat. No. 4,230,688, Oct. 28, 1980 to Rawseal et al.

The level of lipophilic compound in the compositions of the invention is generally in the range from about 0.01% to about 10%, preferably from about 0.05% to about 5%, more preferably from about 0.1% to about 3% by weight.

Compositions in the form of toothpastes, denture cleansing liquids and pastes and the like will generally comprise a binder or thickening agent. Binders suitable for use herein include carboxyvinyl polymers, carrageenan, hydroxyethyl cellulose and water soluble salts of cellulose ethers such as sodium carboxymethyl cellulose and sodium carboxymethyl hydroxyethyl cellulose. Natural gums such as gum karaya, xanthan gum, gum arabic, and gum tragacanth can also be used. Colloidal magnesium aluminum silicate or finely divided silica can be used as part of the thickening agent to further improve texture. Binders/thickening agents can be used in an amount from about 0.1% to about 5.0%, preferably from about 0.1 to about 1% by weight of the total composition.

It is also desirable to include some humectant material in a toothpaste to keep the composition from hardening upon exposure to air. Certain humectants can also impart a desirable sweetness to toothpaste compositions. Liquid dentifrice and mouthwashes can also contain a quantity of humectant. Suitable humectants include glycerin, sorbitol, xylitol, polyethylene glycols, propylene glycol, other edible polyhydric alcohols, and mixtures thereof. When present, humectants generally represent from about 10% to about 70%, by weight of the compositions of the invention.

Toothpastes, liquid dentifrices and denture cleansers in liquid or paste form will generally comprise an abrasive polishing material. The abrasive polishing material contemplated for use herein can be any material which does not excessively abrade dentin or denture acrylic. These include, for example, silicas including xerogels, hydrogels, aerogels and precipitates, calcium and magnesium carbonates, calcium ortho-, pyro- meta- and polyphosphates such as dicalcium orthophosphate dihydrate, calcium pyrophosphate, tricalcium phosphate, and calcium polymetaphosphate, insoluble sodium polymetaphosphate, alumina and hydrates thereof such as alpha alumina trihydrate, aluminosilicates such as calcined aluminium silicate and aluminium silicate, magnesium and zirconium silicates such as magnesium trisilicate and thermosetting polymerised resins such as particulate condensation products of urea and formaldehyde, polymethylmethacrylate, powdered polyethylene and others such as disclosed in U.S. Pat. No. 3,070,510, Dec. 25, 1962.

## US 6,294,154 B1

5

Mixtures of abrasives can also be used. The abrasive polishing materials generally have an average particle size of from about 0.1 to about 30 microns, preferably from about 5 to 15 microns.

Silica dental abrasives of various types offer exceptional dental cleaning and polishing performance without unduly abrading tooth enamel or dentin. The silica abrasive can be precipitated silica or silica gels such as the silica xerogels described in Pader et al., U.S. Pat. No. 3,538,230, issued Mar. 2, 1970 and DiGiulio, U.S. Pat. No. 3,862,307, Jun. 21, 1975, for example silica xerogels marketed under the trademark "Sylloid" by W.R. Grace & Company, Davison Chemical Division. Suitable precipitated silica materials include those marketed by the J.M. Huber Corporation under the trademark, "Zeodent", particularly the silica carrying the designation "Zeodent 119". These silica abrasives are described in U.S. Pat. No. 4,340,583, Jul. 29, 1982.

Highly preferred herein from the viewpoint of providing good cleansing performance combined with excellent compatibility with the antiplaque agent are calcium carbonate abrasives.

The abrasive is generally present in dentifrice formulations of the invention at a level of from about 10% to about 70%, preferably from about 15% to about 25% by weight.

The present compositions can also contain surfactants. Suitable surfactants are those which are reasonably stable and foam throughout a wide pH range, including non-soap anionic, nonionic, cationic, zwitterionic and amphoteric organic synthetic detergents. Many of these suitable agents are disclosed by Gieske et al. in U.S. Pat. No. 4,051,234, Sep. 27, 1977.

Examples of suitable surfactants include alkyl sulfates; condensation products of ethylene oxide with fatty acids, fatty alcohols, fatty amides, polyhydric alcohols (e.g. sorbitan monostearate, sorbitan oleate), alkyl phenols (e.g. Tergitol) and polypropyleneoxide or polyoxybutylene (e.g. Pluronics); amine oxides such as dimethyl cocamine oxide, dimethyl lauryl amine oxide and cocoalkyldimethyl amine oxide (Aromox); polysorbates such as Tween 40 and Tween 80 (Hercules); sorbitan stearates, sorbitan monooleate, etc.; sarcosinates such as sodium cocoylsarcosinate, sodium lauroyl sarcosinate (Hampsyl-95 ex W.R. Grace); cationic surfactants such as cetyl pyridinium chloride, cetyl trimethyl ammonium bromide, di-isobutyl phenoxy ethoxy ethyl-dimethyl benzyl ammonium chloride and coconut alkyl trimethyl ammonium nitrate.

A soluble fluoride ion source can also be incorporated in the present compositions. The soluble fluoride ion source is used in amounts sufficient to provide from about 50 to about 3500 ppm of the fluoride ion. Preferred fluorides are sodium fluoride, stannous fluoride, indium fluoride, zinc ammonium fluoride, tin ammonium fluoride, calcium fluoride and sodium monofluorophosphate. Norris et al., U.S. Pat. No. 2,946,735, issued Jul. 26, 1960 and Widder et al., U.S. Pat. No. 3,678,154, issued Jul. 18, 1972 disclose such salts as well as others.

The present compositions can also include an anti-calculus agent. Suitable anti-calculus agents include the di- and tetra-alkali metal pyrophosphates as set out in EP-A-097476. Specific salts include tetra alkali metal pyrophosphate, dialkali metal diacid pyrophosphate, trialkali metal monoacid pyrophosphate and mixtures thereof, wherein the alkali metals are sodium or potassium. The salts are useful in both their hydrated and unhydrated forms. The amount of pyrophosphate salt useful in these compositions is any effective amount and is generally enough to provide in composition at least 1.0%  $P_2O_7^{4-}$ , preferably from about

6

1.5% to about 10%, more preferably from about 3% to about 6% by weight of composition. The pyrophosphate salts are described in more detail in Kirk & Othmer, *Encyclopedia of Chemical Technology*, Second Edition, Volume 15, Interscience Publishers (1968).

Other anti-calculus agents suitable herein are zinc salts. Zinc salts are disclosed in U.S. Pat. No. 4,100,269, U.S. Pat. No. 4,416,867, U.S. Pat. No. 4,425,325 and U.S. Pat. No. 4,339,432. A preferred agent of the zinc variety is zinc citrate. Zinc compounds can be present in amounts sufficient to provide from about 0.01% to about 4%, preferably from about 0.05% to about 1% by weight of zinc ion.

Other suitable anti-calculus agents include the synthetic anionic polymers (including polyacrylates and copolymers of maleic anhydride or acid and methyl vinyl ether (eg Gantrez) as described in U.S. Pat. No. 4,627,977, polyamino propane sulfonic acid, polyphosphates (eg tripolyphosphate, hexametaphosphate), diphosphonates (eg EHDP, AHP), polypeptides (eg polyaspartic and polyglutamic acids), and mixtures thereof.

Sweetening agents which can be used include aspartame, acesulfame, saccharin, dextrose, levulose and sodium cyclamate. Sweetening agents are generally used at levels of from about 0.005% to about 2% by weight of composition.

Other optional components for use herein include water-soluble antibacterial agents, such as chlorhexidine digluconate, quaternary ammonium antibacterial compounds and water-soluble sources of certain metal ions such as zinc, copper, silver and stannous (e.g., zinc, copper and stannous chloride, and silver nitrate); pigments such as titanium dioxide; orally acceptable dyes/colorants such as FD&C Blue #1, FD&C Yellow #10, FD&C Red #40; antioxidants, vitamins such as vitamin C and E, other antiplaque agents such as stannous salts, copper salts, strontium salts and magnesium salts; pH adjusting agents, anticaries agents such as urea, calcium glycerophosphate, sodium trimetaphosphate, plant extracts, desensitizing agents for sensitive teeth such as potassium nitrate and potassium citrate, and mixtures thereof.

Typically, mouthwashes comprise a water/alcohol solution, flavor, humectant, sweetener, sudsing agent, and colorant as described above. Mouthwashes can include ethanol at a level of from 0 to 60%, preferably from 5 to 30% by weight.

Denture cleanser compositions of the invention can additionally include one or more bleaching agents, organic peroxyacid precursors, effervescence generators, chelating agents, etc.

The bleaching agent takes the form of an inorganic persalt and can be selected from any of the well-known bleaching agents known for use in denture cleansers such as the alkali metal and ammonium persulfates, perborates, percarbonates and perphosphates and the alkali metal and alkaline earth metal peroxides. Examples of suitable bleaching agents include potassium, ammonium, sodium and lithium persulfates and perborate mono- and tetrahydrates, sodium pyrophosphate peroxyhydrate and magnesium, calcium, strontium and zinc peroxides. Of these, however, the alkali metal persulfates, perborates and mixtures thereof are preferred for use herein, highly preferred being the alkali metal perborates. Indeed, it is a feature of the invention that the tablet compositions herein will provide excellent antimicrobial activity even in the absence of alkali metal persulfates.

The amount of bleaching agent in the total composition is generally from about 5 to about 70% preferably from about 10% to about 50%. In compositions comprising a mixture of alkali metal persulfates and perborates, the overall persul-

3,5,5-trimethylhexanoyloxybenzoate, sodium 2-ethylhexanoyl oxybenzenesulfonate, sodium nonanoyl oxybenzene sulfonate and sodium octanoyl oxybenzenesulfonate, the acyloxy group in each instance preferably being p-substituted;

b) Ac has the formula  $R_3(AO)_mXA$  wherein  $R_3$  is a linear or branched alkyl or alkylaryl group containing from 6 to 20, preferably from 6 to 15 carbon atoms in the alkyl moiety,  $R_5$  being optionally substituted by Cl, Br,  $OCH_3$ , or  $OC_2H_5$ , AO is oxyethylene or oxypropylene, m is from 0 to 100, X is 0,  $NR_4$  or  $CO-NR_4$ , and A is  $CO$ ,  $CO-CO$ ,  $R_6-CO$ ,  $CO-R_6-CO$ , or  $CO-NR_4-R_6-CO$  wherein  $R_4$  is  $C_1-C_4$  alkyl and  $R_6$  is alkylene, alkenylene, arylene or alkarylene containing from 1 to 8 carbon atoms in the alkylene or alkenylene moiety. Bleach activator compounds of this type include carbonic acid derivatives of the formula  $R_3(AO)_mOCOL$ , succinic acid derivatives of the formula  $R_3OCO(CH_2)_2COL$ , glycolic acid derivatives of the formula  $R_3OCH_2COL$ , hydroxypropionic acid derivatives of the formula  $R_3OCH_2CH_2COL$ , oxalic acid derivatives of the formula  $R_3OCOCOL$ , maleic and fumaric acid derivatives of the formula  $R_3OCOCH=CHCOL$ , acyl aminocaproic acid derivatives of the formula  $R_3CONR_1(CH_2)_6COL$ , acyl glycine derivatives of the formula  $R_3CONR_1CH_2COL$ , and amino-6-oxocaproic acid derivatives of the formula  $R_3N(R_1)CO(CH_2)_4COL$ . In the above, m is preferably from 0 to 10, and  $R_3$  is preferably  $C_6-C_{12}$ , more preferably  $C_6-C_{10}$  alkyl when m is zero and  $C_9-C_{15}$  when m is non-zero. The leaving group L is as defined above.

5) Acyl-cyanurates, such as triacetyl- or tribenzoylcyanurates, as disclosed in US patent specification No. 3,332,882.

6) Optionally substituted anhydrides of benzoic or phthalic acid, for example, benzoic anhydride, m-chlorobenzoic anhydride and phthalic anhydride.

Of all the above, preferred are organic peracid precursors of types 1(c) and 4(a).

Where present, the level of peroxyacid bleach precursor by weight of the total composition is preferably from about 0.1% to about 10%, more preferably from about 0.5% to about 5% and is generally added in the form of a bleach 45 precursor agglomerate.

The bleach precursor agglomerates preferred for use herein generally comprise a binder or agglomerating agent in a level of from about 5% to about 40%, more especially from about 10% to about 30% by weight thereof. Suitable agglomerating agents include polyvinylpyrrolidone, poly (oxyethylene) of molecular weight 20,000 to 500,000, polyethyleneglycols of molecular weight of from about 1000 to about 50,000, Carbowax having a molecular weight of from 4000 to 20,000, nonionic surfactants, fatty acids, sodium carboxymethyl cellulose, gelatin, fatty alcohols, phosphates and polyphosphates, clays, aluminosilicates and polymeric polycarboxylates. Of the above, polyethyleneglycols are highly preferred, especially those having molecular weight of from about 1,000 to about 30,000, preferably 2000 to about 10,000.

Preferred from the viewpoint of optimum dissolution and pH characteristics are bleach precursor agglomerates which comprise from about 10% to about 75%, preferably from about 20% to about 60% by weight thereof of peroxyacid bleach precursor, from about 5% to about 60% preferably from about 5% to about 50%, more preferably from about

10% to about 40% of a (bi) carbonate/acid effervescent couple, from about 0% to about 20% of a peroxoboroate, and from about 5% to about 40%, preferably from about 10% to about 30% of an agglomerating agent.

5 The final bleach precursor granules desirably have an average particle size of from about 500 to about 1500, preferably from about 500 to about 1,000  $\mu\text{m}$ , this being valuable from the viewpoint of optimum dissolution performance and aesthetics. The level of bleach precursor 10 agglomerates, moreover, is preferably from about 1% to about 20%, more preferably from about 5% to about 15% by weight of composition.

The denture cleansing compositions of the invention can be in paste, tablet, granular or powder form, although 15 tablet-form compositions are highly preferred herein. Compositions in tablet form can be single or multiple layered tablets.

Denture cleansing compositions of the invention can be supplemented by other usual components of such 20 formulations, especially surfactants, chelating agents, enzymes, flavorants, physiological cooling agents, antimicrobial compounds, dyestuffs, sweeteners, tablet binders and fillers, foam depressants such as dimethylpolysiloxanes, foam stabilizers such as the fatty acid sugar esters, preservatives, lubricants such as talc, magnesium stearate, finely divided amorphous pyrogenic silicas, etc. The free moisture content of the final composition is desirably less than about 1% and especially less than about 0.5%.

Tablet binders and fillers suitable for use herein include 25 polyvinylpyrrolidone, poly (oxyethylene) of molecular weight 20,000 to 500,000, polyethyleneglycols of molecular weight of from about 1000 to about 50,000, Carbowax having a molecular weight of from 4000 to 20,000, nonionic surfactants, fatty acids, sodium carboxymethyl cellulose, gelatin, fatty alcohols, clays, polymeric polycarboxylates, sodium carbonate, calcium carbonate, calcium hydroxide, magnesium oxide, magnesium hydroxide carbonate, sodium sulfate, proteins, cellulose ethers, cellulose esters, polyvinyl alcohol, alginic acid esters, vegetable fatty materials of a pseudocolloidal character. Of the above, polyethyleneglycols are highly preferred, especially those having molecular weight of from about 1,000 to about 30,000, preferably from about 12,000 to about 30,000.

The surface active agent used in the denture cleansing 30 compositions of the invention can be selected from the many available that are compatible with the other ingredients of the denture cleanser, both in the dry state and in solution. Such materials are believed to improve the effectiveness of the other ingredients of the composition by aiding their penetration into the interdental surfaces. Also, these materials aid in the removal of food debris attached to the teeth. Between 0.1 and 5 percent by weight of the dry composition of a dry powder or granular anionic surface active agent, such as sodium lauryl sulfate, sodium N-lauroylsarcosinate, sodium lauryl sulfoacetate or dioctyl sodium sulfosuccinate 35 or ricinoleyl sodium sulfosuccinate, may, for example, be included in the composition and preferably the surface active agent comprises between 0.5 and 4 percent of the composition.

Suitable cationic, non-ionic and ampholytic surface active 40 agents include, for example, quaternary ammonium compounds such as cetyltrimethylammonium bromide, condensation products of alkylene oxides such as ethylene or propylene oxide with fatty alcohols, phenols, fatty amines or fatty acid alkanolamides, the fatty acid alkanolamides themselves, esters of long-chained ( $C_8-C_{22}$ ) fatty acids with polyalcohols or sugars, for example glycerylmonostearate or

11

saccharosemonolaurate or sorbitolpolyoxyethylenemono or di-stearate, betaines, sulphobetaines or long-chain alkylamino-carboxylic acids.

Chelating agents beneficially aid cleaning and bleach stability by keeping metal ions, such as calcium, magnesium, and heavy metal cations in solution. Examples of suitable chelating agents include sodium tripolyphosphate, sodium acid pyrophosphate, tetrasodium pyrophosphate, aminopolycarboxylates such as nitrilotriacetic acid and ethylenediamine tetracetic acid and salts thereof, and polyphosphonates and aminopolyphosphonates such as hydroxyethanephosphonic acid, ethylenediamine tetramethyleneephosphonic acid, diethylenetriaminepentamethyleneephosphonic acid and salts thereof. The chelating agent selected is not critical except that it must be compatible with the other ingredients of the denture cleanser when in the dry state and in aqueous solution. Advantageously, the chelating agent comprises between 0.1 and 60 percent by weight of the composition and preferably between 0.5 and 30 percent. Phosphonic acid chelating agents, however, preferably comprise from about 0.1 to about 1 percent, preferably from about 0.1% to about 0.5% by weight of composition.

Enzymes suitable for use herein are exemplified by proteases, alkalases, amylases, lipases, dextranases, mutanases, glucanases etc.

The following Examples further describe and demonstrate the preferred embodiments within the scope of the present invention.

## EXAMPLES I TO V

The following are representative denture cleansing tablets according to the invention. The percentages are by weight of the total tablet. The tablets are made by compressing a mixture of the granulated components in a punch and dye tabletting press at a pressure of about  $10^5$  kPa.

	I	II	III	IV	V
Malic Acid	12	10	15	—	14
Citric Acid	—	10	—	15	—
Sodium Carbonate	10	8	10	6	10
Sulphamic Acid	5	—	—	3	3
PEG 20,000	—	3	7	8	5
PVP 40,000	6	3	—	—	—
Sodium Bicarbonate	22	25.2	25	13.9	23
Sodium Perborate Monohydrate	15	12	16	30	15
Potassium Monopersulphate	15	18	13	—	14
Pyrogenic Silica	—	0.3	0.1	0.1	—
Talc	2	—	—	—	—
EDTA	—	—	1	—	3
EDTMP <sup>1</sup>	1	—	—	1	—
Flavor <sup>5</sup>	2	1	2	1	2
Abil EM90 <sup>4</sup>	1	1.5	5	10	1
Bleach Precursor Agglomerate	9	8	10	12	10
Bleach Precursor Agglomerate	—	—	—	—	—
TAED <sup>7</sup>	2	—	4	5	2.5
TMHOS <sup>3</sup>	2	3	—	—	—
Sulphamic Acid	2	2	2	2	3.5
Sodium Bicarbonate	0.5	0.2	0.2	0.5	2
PEG 6000	2.5	2	2.4	2.5	1.5
Dye	—	0.8	1.4	2	0.5

<sup>1</sup> Ethylenediaminetetramethylenephosphonic acid

### <sup>2</sup>. Tetraacetylethylene diamine

<sup>3</sup>. Sodium 3,5,5-trimethylhexanoyloxybenzene sulfonate

#### **4. Cetyl dimethicone copolyol**

#### <sup>5</sup>. Peppermint-based flavor

In Examples I to V above, the overall tablet weight is 3 g; diameter 25 mm.

The denture cleansing tablets of Examples I to V display improved antiplaque cleansing and anti-bacterial activity.

12

together with excellent cohesion and other physical and in-use performance characteristics.

## EXAMPLES VI TO VIII

The following are representative toothpaste/denture cleansing pastes according to the invention. The percentages are by weight of total composition.

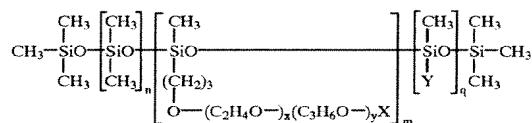
	VI	VII	VIII
10			
Calcium Carbonate	20	25	15
Glycerine	10	12	8
Sodium CMC	3.5	3	4
Titanium Dioxide	0.7	0.5	0.6
Methyl/Propyl Parabens	0.1	0.1	0.1
Sodium Saccharin	0.3	0.4	0.2
Flavor <sup>5</sup>	1	1	2
Abil EM90 <sup>4</sup>	1	1.5	0.5
Trichlosan	—	0.5	—
Water		To 100	
20			

The toothpastes/denture cleansing pastes of examples VI to VIII display improved antiplaque, flavor impact and anti-bacterial activity together with excellent cleansing characteristics.

What is claimed is:

What is claimed is:

1. An oral composition in the form of a toothpaste, powder, liquid dentifrice, mouthwash, denture cleanser, chewing gum or candy comprising a lipophilic compound selected from flavorants, physiological cooling agents and antimicrobial compounds and a dimethicone copolyol selected from alkyl- and alkoxy-dimethicone copolyols having the formula (I):



wherein X is selected from hydrogen, alkyl, alkoxy and acyl groups having from about 1 to about 16 carbon atoms, Y is selected from alkyl and alkoxy groups having from about 8 to about 22 carbon atoms, n is from about 0 to about 200, m is from about 1 to about 40, q is from about 1 to about 100, the molecular weight of the residue  $(C_2H_4O)_x(C_3H_6O)_y$ , X is from about 50 to about 2000, and x and y are such that the weight ratio of oxyethylene:oxypropylene is from about 100:0 to about 0:100.

**2.** A composition according to claim 1 wherein the dimethicone copolyol is selected from C<sub>12</sub> to C<sub>20</sub> alkyl dimethicone copolyols and mixtures thereof.

3. A composition according to claim 1 wherein the dimethicone copolyol is cetyl dimethicone copolyol.

4. A composition according to claim 1 comprising from about 0.01% to about 25% by weight of the dimethicone copolyol.

5. A composition according to claim 4 wherein the lipophilic compound comprises a flavorant comprising one or more flavor components selected from wintergreen oil, oregano oil, bay leaf oil, peppermint oil, spearmint oil, clove oil, sage oil, sassafras oil, lemon oil, orange oil, anise oil, benzaldehyde, bitter almond oil, camphor, cedar leaf oil, marjoram oil, citronella oil, lavender oil, mustard oil, pine oil, pine needle oil, rosemary oil, thyme oil, cinnamon leaf

US 6,294,154 B1

**13**

6. A composition according to claim 4 wherein the lipophilic compound comprises an antimicrobial compound selected from thymol, menthol, triclosan, 4-hexylresorcinol, phenol, eucalyptol, benzoic acid, benzoyl peroxide, butyl paraben, methyl paraben, propyl paraben, salicylamides, and mixtures thereof.

7. A composition according to claim 4 comprising from about 10% to about 70% by weight of a dental abrasive selected from silica, alumina, aluminosilicates, magnesium and zirconium silicates, calcium ortho-, pyro- meta- and

**14**

polyphosphates, calcium and magnesium carbonates, insoluble metaphosphates and thermosetting polymerised resins.

8. A composition according to claim 4 comprising an amount of a fluoride ion source sufficient to provide from 50 ppm to 3500 ppm of fluoride ions.

9. A composition according to claim 4 comprising from about 0.1% to about 1% by weight of a binder.

10. A composition according to claim 4 comprising from about 0.1% to about 5% by weight of the dimethicone copolyol.

\* \* \* \* \*

## US 6,294,154 B1

7

fate:perborate ratio is suitably from about 5:1 to about 1:5, more especially from about 2:1 to about 1:2.

The denture cleansing compositions can also incorporate an effervescence generator, ie a material which in the presence of water releases carbon dioxide or oxygen with effervescence. The effervescence generator can be selected from generators which are effective under acid, neutral or alkaline pH conditions, but preferably it consists of a combination of a generator which is effective or most effective under acid or neutral pH conditions and a generator which is effective or most effective under alkaline pH conditions. Effervescence generators which are effective under acid or neutral pH conditions include a combination of at least one alkali metal carbonate or bicarbonate, such as sodium bicarbonate, sodium carbonate, sodium sesquicarbonate, potassium carbonate, potassium bicarbonate, or mixtures thereof, in admixture with at least one non-toxic, physiologically-acceptable organic acid, such as tartaric, fumaric, citric, malic, maleic, gluconic, succinic, salicylic, adipic or sulphamic acid, sodium fumarate, sodium or potassium acid phosphates, betaine hydrochloride or mixtures thereof. Of these, malic acid is preferred. Effervescence generators which are effective under alkaline pH conditions include persalts such as alkali and alkaline earth metal peroxoborates as well as perborates, persulphates, percarbonates, perphosphates and mixtures thereof as previously described, for example, a mixture of an alkali metal perborate (anhydrous, mono- or tetrahydrate) with a monopersulphate such as Caroat® marketed by EI du Point de Nemours Co. and which is a 2:1:1 mixture of monopersulphate, potassium sulphate and potassium bisulphate and which has an active oxygen content of about 4.5%.

In preferred denture cleansing compositions in tablet form, the effervescence generator takes the form of a solid base material which in the presence of water releases carbon dioxide or oxygen with effervescence. Suitably, the solid base material incorporates a (bi)carbonate/acid effervescent couple optionally in combination with a perborate/persulphate oxygen effervescence generator. The combination of generators is valuable for achieving optimum dissolution characteristics and pH conditions for achieving optimum cleaning and antimicrobial activity. The (bi) carbonate components generally comprise from about 5% to about 65%, preferably from about 25% to 55% of the total composition; the acid components generally comprise from about 5% to about 50%, preferably from about 10% to about 30% of the total composition.

The denture cleansing compositions of the invention can be supplemented by other known components of such formulations. An especially preferred additional component is an organic peroxyacid precursor, which in general terms can be defined as a compound having a titre of at least 1.5 ml of 0.1N sodium thiosulfate in the following peracid formation test.

A test solution is prepared by dissolving the following materials in 1000 mls distilled water:

sodium pyrophosphate

(Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>.10H<sub>2</sub>O) 2.5 g

sodium perborate

(NaBO<sub>2</sub>.H<sub>2</sub>O<sub>2</sub>.3H<sub>2</sub>O) having

10.4% available oxygen 0.615 g

sodium dodecylbenzene

sulphonate 0.5 g

To this solution at 60° C. an amount of activator is added such that for each atom of available oxygen present one molecular equivalent of activator is introduced.

The mixture obtained by addition of the activator is vigorously stirred and maintained at 60° C. After 5 minutes

8

from addition, a 100 ml portion of the solution is withdrawn and immediately pipetted onto a mixture of 250 g cracked ice and 15 ml glacial acetic acid. Potassium iodide (0.4 g) is then added and the liberated iodine is immediately titrated with 0.1 N sodium thiosulphate with starch as indicator until the first disappearance of the blue colour. The amount of sodium thiosulphate solution used in ml is the titre of the bleach activator.

The organic peracid precursors are typically compounds containing one or more acyl groups, which are susceptible to perhydrolysis. The preferred activators are those of the N-acyl or O-acyl compound type containing a acyl radical R—CO wherein R is a hydrocarbon or substituted hydrocarbon group having preferably from about 1 to about 20 carbon atoms. Examples of suitable peracid precursors include:

- 1) Acyl organoamides of the formula RCONR<sub>1</sub>R<sub>2</sub>, where RCO is carboxylic acyl radical, R<sub>1</sub> is an acyl radical and R<sub>2</sub> is an organic radical, as disclosed in U.S. Pat. No. 3,117,148. Examples of compounds falling under this group include:
  - a) N,N-diacyl aniline and N-acetylphthalimide;
  - b) N-acylhydantoins, such as N,N'-diacetyl-5,5-dimethylhydantoin;
- c) Polyacylated alkylene diamines, such as N,N,N'N'-tetraacetylene-1,4-diamine (TAED) and the corresponding hexamethylene-1,6-diamine (TAHD) derivatives, as disclosed in GB-A-907,356, GB-A-907,357 and GB-A-907,358;
- d) Acylated glycolurils, such as tetraacetylglycoluril, as disclosed in GB-A-1,246,338, GB-A-1,246,339 and GB-A-1,247,429.
- 2) Acylated sulphonamides, such as N-methyl-N-benzoyl-menthane sulphonamide and N-phenyl-N-acetyl menthane sulphonamide, as disclosed in GB-A-3,183,266.
- 3) Carboxylic esters as disclosed in GB-A-836,988, GB-A-963,135 and GB-A-1,147,871. Examples of compounds of this type include phenyl acetate, sodium acetoxy benzene sulphonate, trichloroethylacetate, sorbitol hexaacetate, fructose pentaacetate, p-nitrobenzaldehyde diacetate, isopropenyl acetate, acetyl aceto hydroxamic acid, and acetyl salicylic acid. Other examples are esters of a phenol or substituted phenol with an alpha-chlorinated lower aliphatic carboxylic acid, such as chloroacetylphenol and chloroacetylsalicylic acid, as disclosed in U.S. Pat. No. 3,130,165.
- 4) Carboxylic esters having the general formula Ac L wherein Ac is the acyl moiety of an organic carboxylic acid comprising an optionally substituted, linear or branched C<sub>6</sub>—C<sub>20</sub> alkyl or alkenyl moiety or a C<sub>6</sub>—C<sub>20</sub> alkyl-substituted aryl moiety and L is a leaving group, the conjugate acid of which has a pKa in the range from 4 to 13, for example oxybenzenesulfonate or oxybenzoate. Preferred compounds of this type are those wherein:
  - a) Ac is R<sub>3</sub>—CO and R<sub>3</sub> is a linear or branched alkyl group containing from 6 to 20, preferably 6 to 12, more preferably 7 to 9 carbon atoms and wherein the longest linear alkyl chain extending from and including the carbonyl carbon contains from 5 to 18, preferably 5 to 10 carbon atoms, R<sub>3</sub> optionally being substituted (preferably alpha to the carbonyl moiety) by Cl, Br, OCH<sub>3</sub> or OC<sub>2</sub>H<sub>5</sub>. Examples of this class of material include sodium 3,5,5-trimethylhexanoyloxybenzene sulfonate, sodium